APPLICATION OF 2-D AND DIPOLAR DEPHASING ^{13}C NMR TECHNIQUES TO THE STUDY OF STRUCTURAL VARIATIONS IN COAL MACERALS

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INTRODUCTION

Coal has been described as an organic rock. In order to better utilize coal supplies, however, the chemical structure of coal needs to be known in much greater detail so that methods can be developed to convert coal to a clean burning liquid or gaseous fuel.

Coal is known to be a physically heterogeneous substance with inorganic mineral matter mixed randomly in the organic material. The organic matter is further subdivided into maceral groups which reflect the floristic assemblages available at the time of the formation of the coal measures. The chemical structural detail of the organic components of these materials is not well known, even though researchers have been working for decades on structure analysis. Of interest is the nature of the carbon skeleton including the aromatic and aliphatic groups; the level, type and role of oxygen, nitrogen, and sulfur; the type and extent of cross-linking; and the molecular weight distribution of the macromolecules.

Useful reviews and monographs published on coal structural analysis include works by Van Krevelan (1), Ignasiak (2), Tingey and Morrey (3), Davidson (4), Larsen (5), and Karr (6). These reports indicate the following: Coal is a highly aromatic substance (65-90% aromatic carbon, variable with rank but with few coals having aromaticities lower than 50%), with clusters of condensed rings (up to approximately four rings); the aliphatic part of the coal appears to be mostly hydroaromatic rings and short aliphatic chains connecting the aromatic clusters; the oxygen has been found in the form of phenols, quinones, ethers, and carboxylic acids, but less detail is known about the nature of the organic sulfur or nitrogen.

The study of the aromaticity of coal has included infrared spectroscopy (7) and various chemical methods (8,9), but the most promising analytical tool appears to be cross-polarization magic angle sample spinning nuclear magnetic resonance spectroscopy (CP/MAS C-13 NMR). This technique, initially developed by Pines, et al (10), has been successfully applied to coals by several workers in order to obtain aromatic-to-aliphatic ratios (11-14) (f_a). There is evidence that further structural information on coals and coal macerals can be gained from the CP/MAS C-13 NMR experiments (15-19). The aliphatic part of coal has also been characterized by a novel chemical method involving a trifluoroacetic acid/aqueous hydrogen peroxide oxidation of the aromatic rings to yield aliphatic acids and diacids (20). Chemical test results may be spurious, however, due to the severity of the reaction conditions and the insoluble and heterogeneous nature of coals.

CP/MAS ^{13}C NMR offers a powerful non-destructuve tool for the analysis of carbonaceous solids. Depending on the nature of the carbonaceous material and the concomitant resolution obtainable, a wide range of structural information can be obtained. In complex organic sediments, the diversity of structural components leads to broad bands that frequently lack detail. However, employing multiple pulse techniques, it is possible to obtain additional structural information. The dipolar dephasing technique reported by Opella (26,27) discriminates protonated from nonprotonated carbons in a CP/MAS spectrum on the basis of the ^{1}H-^{13}C dipolar interaction. Hagaman and Woody (28) have reported the spectra of Illinois No. 6 coal.

We wish to report data on a series of whole coals and coal macerals using conventional CP/MAS, dipolar dephasing, and 2-D dipolar dephasing techniques. These data provide a wealth of new structural information and demonstrate that multiple pulse and 2-D spectroscopic techniques can be utilized on complex carbonaceous materials. We also report data obtained on maceral samples separated by the density gradient centrifugation method which separates coal maceral groups according to density.

EXPERIMENTAL

All ^{13}C NMR CP/MAS spectra were obtained on a Bruker CXP-100 instrument equipped with a Z32DR ^{13}C-MASS superconducting magnet probehead for proton enhanced magic angle spinning experiments (CP/MAS). Samples were packed in carefully prepared rotors machined from boron nitride (body material) and Kel-F (spinner head material) in Andrew-Beams type rotors (22). Boron nitride is used as the body material because of its good tensil strength and its resistance to deformation at high spinning speeds, whereas the Kel-F material is used for the rotor head material because of its better resistance to wearing as it comes into occasional contact with the stator assembly during start ups and stops. Both materials are free of carbon and hydrogen which would cause extraneous resonance signals and decoupler heating problems. The spinning speed was slightly in excess of 4 KHz to avoid complications due to overlapping of spining side bands with other spectral components. The carbon-proton cross polarization time was 1.5 msec and the cycle time was 0.3 seconds. Experiments performed at this laboratory have shown that such short cycle times are indeed feasible with coals because of the inherent free radical induced short relaxations times (23). Each spectra resulted from averaging 10,000 repetitions on samples of approximately 100 mg size. The dipolar dephasing experiments involved a 40 μsec delay inserted between the contact time and the acquisition period. It is well known that this delay period will decrease the signal intensities of <u>all</u> carbon peaks compared to their intensities in the normal CP/MAS spectrum due to T_2 relaxation effects; however, no effort has been made to correct for this decrease in intensity to effect a material balance between compared spectra since it is assumed that the decrease in intensity of the nondipolar dephased carbon-13 peak is small. Chemical shifts are reported referenced to TMS. Hexamethyl benzene was used as an external referencing material. A rotor of the reference solid is used to adjust the magic angle and the carbon/proton power levels for the Hartman Hahn condition such that the aromatic and aliphatic carbon peaks are of essentially equal intensities. The coal samples were then substituted using the same rotor without changing any resolution or referencing parameters. The upfield peak of hexamathylbenzene is presumed to be at 18 ppm from TMS.

COAL MACERALS AND MACERAL SEPARATION

The coals designated as PSOC-2 and PSOC-858 were obtained from the Coal Data Bank at the Pennsylvania State University. The maceral groups from this coal were separated by the density gradient centrifugation technique described by Dyrkacz (24,25). The samples designated by PSMC-67, -19, -34, -43, -47, and -53 were vitrinite concentrates obtained from Professor Alan Davis at Penn State and the analytical and CP/MAS data have been previously reported (16). The British maceral concentrates designated as Aldwarke, Silkstone, Teversil, Dunsil, Woolley, Wheatley Lime, Markham Main, and North Celyen were obtained from Professor Peter Given at Penn State and the analytical data on these coals are given in Table III. The samples were provided to Professor Given by the British National Coal Board and were stored under nitrogen since their preparation.

RESULTS AND DISCUSSION

We have recently established in our laboratory the capability to separate coal macerals by the density gradient centrifugation technique (DGC) described by Dyrkacz (24,25). The DGC fractogram of PSOC-2 is presented in Figure 1 indicating the density delineation of the three maceral groups. The mean densities indicated in the Figure correspond to the liptinite (largely sporinite, see Table I) vitrinite and inertinite maceral fractions. The actual density ranges for the six different samples studied are used as labels for each spectrum illustrated in Figure 2 along with the separate f_a values. This coal contains essentially no liptinite and hence exhibits only two peaks corresponding to vitrinite and inertinites (semi-fusinite and fusinite). The stacked CP/MAS spectra of the PSOC-2 whole coal and the sporinite, three vitrinite, and two inertinite fractions separated by the DGC technique are given in Figure 2. Note the variation in the band shapes in the aliphatic regions of the vitrinite and inertinite maceral groups. These data clearly indicate that additional structural information is obtainable from studies of coal maceral groups which have been separated from a given coal as previously reported (17,18). Even within the three vitrinite samples, large variations in spectral characteristics indicate structural differences among macerals of small density variance. Similar structural changes are observed in the vitrinite maceral group for PSOC-858.

Additional structural information can be obtained by means of the dipolar dephasing technique reported by Opella (26,27) which discriminates protonated from nonprotonated carbons in a CP/MAS spectrum on the basis of the ^1H-^{13}C dipolar interaction. Hagaman and Woody (28) have reported the spectra of Illinois No. 6 coal by employing this technique. In model compounds, Alemany (29) has observed that a 40-μs interruption in the proton decoupling will cause all of the CH and CH_2 resonances to vanish, while the intensity of the nonprotonated carbons experience only minor attenuation (ca. 10-20%). The dephasing of a methyl group is more complex but approximately 50% of the methyl carbon signal is still observed after a 40 sec dephasing delay. Hence, by appropriately varying the interruption of the decoupler one can differentiate among methine/methylene, methyl and nonprotonated carbons. Typical results are given in Figure 3 for the Aldwarke Silkstone exinite. The fraction of the carbon in the sample which is aromatic and nonprotonated, f_a^N, is obtained by comparing the relative intensities of the aromatic region of the spectra with decoupler pulse delays of 0 and 40 sec before data acquisition. The fraction of protonated aromatic carbon is then f_a^H; thus $f_a^H + f_a^N = f_a$. Using a solvent refined coal tar for which high resolution ^1H and ^{13}C NMR data were taken, Wilson (30) has obtained values of f_a, and f_a^H in the solid tar. These values agree nicely with those corresponding values obtained for the dissolved tar. (f_a = 0.62, 0.62; f_a^H = 0.24, 0.23 for the solid and dissolved solvent refined coal, respectively).

Dipolar dephasing data (26,17) have been acquired on 36 coal and maceral samples and some of the results are given in Table II. The data are indicative again of the highly variable structure found in coal samples. The values designated as f_s^S and f_a^B are the fraction of aromatic carbon atoms which are substituted and those which are bridgehead carbons respectively. This separation is based strictly on the chemical shift range of the nonprotonated aromatic carbons; i.e., in the dipolar dephasing spectrum, it is assumed that nonprotonated carbon resonance shifts greater than 133 ppm are substituted while those with chemical shifts less than 133 ppm are bridgeheads. This arbitrarily chosen chemical shift value has, of course, been assigned from previous experience using the spectral assignments of known compounds. The values found in the last column of Table II reflect the fraction of the aliphatic region which is both nonprotonated carbons and methyl group carbons and has been designated as f_s^*. If the carbon resonances due to these two differing types of species are distinctive, they can be further identified with the use of 2-dimensional dipolar dephasing techniques based on their differing dephasing rates. Carbon-13 data obtained on a series of British maceral concentrates are also expressed in Table II. Further analytical data for these concentrates are found in Table III. The data found in this table has been supplied by the Coal Survey National Coal Board. The Woolley Wheatly Lime sample is 93% fusinite while the Teversal Dunsil concentrate is 80% semifusinite with 13% fusinite. The Aldwarke Silkstone sample contains 43% semifusinite and 43% fusinite. The petrographic analysis of PSOC-2 reveals nearly equivalent amounts of fusinite, semifusinite, micrinite, and macrinite (6.8, 8.1, 7.5 and 8.5% respectively in the whole coal). The differences in f_a^H values for these samples are greater than the experimental error and these differences suggest that NMR techniques may be useful in characterizing the chemical structural differences between inertinite macerals.

The use of 2-D ^{13}C NMR techniques in liquids has progressed from a novelty to a very useful analytical tool. Even though the use of 2-D pulse techniques on solids is not as advanced, experiments on simple organic compounds have appeared in the literature (31). The principal value of 2-D spectroscopy in solid CP/MAS studies of coal and related macerals lies in the ability of such methods to separate spectral information which in the typical one dimensional case appears as a single resonance. Figure 3 is a 2-D contour plot of the Aldwarke Silkstone exinite maceral exhibiting chemical shift along the F_2 axis. It should be emphasized here that those carbon resonances which extend further along the F_1 axis have larger dipolar dephasing effects working upon them. Such effects can then be graphically used to differentiate between carbons of similar chemical shift but differing proton environments. Figure 5 is a stack plot of the same information found in Figure 3. Spectral traces differ from each other by 977 Hz starting with the top spectrum at zero Hz dipolar dephasing rate.

The capability of measuring directly the fraction of aromatic carbon, f_a relative to total carbon via solid ^{13}C NMR has stimulated considerable interest. The f_a values previously found (32,33) for coal macerals have been consistent with the order fusinite > micrinite > vitrinite > exinite given by Dormans et al (34) for macerals of a specific rank. For the sample set of PSOC-2 and its separated maceral groups, the f_a values found in this study are in the order inertinite > vitrinite > exinite as expected. An interesting observation is that f_a^H, the fraction of the total carbon in the coal that is arc.atic and protonated, decreases in that same order for this series of six macerals. These data imply that there is a significant diversity in the amount of ring substitution and/or cross linking among the aromatic carbons in the various macerals as seen in the estimated values for the fraction of aromatic substituted and bridgehead carbons, f_a^S and f_a^B. An examination of the pure vitrinite series PSMC-67, -19, -34, -43, -47, and -53, which is a suite of samples from a common depositional environment but of varying rank, reveals a similar trend in samples of increasing rank. The CP/MAS data reported earlier (16) exhibited a decrease in functionality with progressing rank (i.e., loss of alkyl and aromatic oxygen groups). The dipolar dephasing data of this report indicate that this loss of functionality leads to a net increase in the fraction of protonated aromatic carbons. Ring condensation reactions alone cannot explain these results as ring condensation would produce an opposite effect. It appears that reactions associated with vitrinite maturation in these samples must also include some ring protonation reactions accompanying ring defunctionalization and the data suggests that these protonation reactions are preferred to ring condensation reactions.

Data on the set of British maceral concentrates, Table I, exhibit trends similar to those noted above. Comparing the f_a^H data on the inertinite fractions from PSOC-2, Woolley Wheatley Lime, Teversal Dunsil, and Aldwarke Silkstone reveals some significant differences between these samples from coals of high volatile bituminous rank (albeit, perhaps from quite different environments).

Carbon resonances arising from both nonprotonated and protonated aromatic carbons may appear at the same frequency under proton decoupling. Yet these two resonances could possess very different relaxation behavior and in a solid could evolve very differently due to local proton dipolar fields which attenuate with the carbon proton distances as $1/r_{CH}^3$. When the spin locking pulse for proton nuclei is turned off, carbons with directly bound protons such as methines and methylenes rapidly dephase in the local proton fields and their spectral response is rapidly diminished. The rapid internal motion of CH_3 groups greatly decreases the effectiveness of methyl protons. Nonprotonated carbons are only dephased by remote and therefore much weaker magnetic fields. This type of response is given in Figure 2 using the pulse sequences first proposed by Rybaczewske et al (31) and popularized by Opella (26,27) for powders. These two spectral traces demonstrate how carbon atoms with protons are significantly attenuated following a 40μsec dephasing time. Thus, the upfield portion of the aromatic peak due to protonated carbons and essentially all of the aliphatic region are attenuated leaving primarily the nonprotonated aromatic carbons and methyl carbons (the two high field peaks in the lower trace which have chemical shift values for aliphatic and aromatic CH_3 carbons). The small vestigial remnant of the once very strong methine/methylene peak appears as the lowest field peak of the three distinct aliphatic peaks. Thus, this spectral response is limited to a subportion of the total spectrum contained in the upper trace.

Thus, otherwise overlapping spectral information has been obtained by employing in a subtle way the differing dipolar properties of the different types of carbons. If this spectral feature is made the basis of a two dimensional, 2-D, FT spectrum, one may simultaneously obtain spectral information on both nonprotonated and protonated carbons directly. Figures 3 and 4 contain such a 2-D spectrum for the Aldwarke Silkstone exinite. In Figure 4 a contour plot of the spectral intensities is given for the rate of dipolar dephasing along the y-axis vs. chemical shift along the x-axis. Thus, the nonprotonated and methyl carbons show steep fall off in the intensity contours while protonated carbons are represented by much broader (along y-axis) spectral responses. Vertical cuts through the 2-D surface along the chemical shift axis are given in Figure 5. Hence, we observe in a more typical format the spectral respose as a function of a dipolar dephasing frequency. For a solid powder the C-H dipole-dipole vectors span all possible orientations and thus zero frequency responses are found for all resonances, albeit the spread in aliphatic response is distributed over such a much greater range of dephasing frequencies as to reduce this part nearly to the noise level. The successive slices in Figure 5 leaves the CH_2 peak persisting to higher dephasing frequencies as would be expected from the data in Figure 3. There is an inverse relationship between the time slices in Figure 3 and the frequency slices in Figure 5. Short times contain information corresponding to larger dephasing frequencies. The three dimensional plot (Figure 6) of the aromatic portion of Figures 4 and 5 helps one to appreciate the above point. Note in the plot sharp peaks corresponding to nonprotonated carbons. This feature is graphically shown in the 3-D portrayal. A single chemical shift slice through the aromatic region, also shown in Figure 5, emphasized the dual nature of the spectral response with a sharp peak resting on a broad base peak. Curve fitting techniques can easily resolve the true components.

Thus, using very sophisticated spectral resolving techniques, important structural information on coal is now available from these techniques for the first time. Hence, multiple pulse/multidimensional spectroscopy offers an exciting new analytical tool for the study of complex materials such as coal and coal macerals.

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TABLE I

Elemental Analysis and Maceral Composition of Coal PSOC-2 Separated by Density Gradient Centrifugation Techniques

Petrographic Analysis (Volume %)	COAL PSOC-2
Liptinites	
Alginites	0.0
Resinite	1.2
Cutinite	1.4
Sporinite	33.6
Vitrinite	29.6
Inertinites	
Micrinite	8.7
Semifusinite	8.3
Fusinite	7.0
Macrinite	7.7
Total Liptinites	36.2
Total Vitrinite	32.1
Total Inertinites	31.7
Elemental Analysis (DMMF %)*	
C	85.49
H	5.56
N	1.46
S	0.62
O (by difference)	6.79
Mineral Matter Content of Coal* (Before Demineralization)	3.82
Vitrinite Reflectance* (Mean maximum)	0.89
Class*	HVAB
Coal Type	Channel Lithotype

* Values reported by Penn State on different samples of the same coal.

TABLE II

Structural Parameters of Coals and Coal Macerals

	H/C	%C (DMMF)	f_a	f_a^H	f_a^N	f_a^B	f_a^S	f_s^H	f_s^*
PSOC-2	0.79	86.61	0.60	0.39	0.21	0.11	0.10	0.36	0.05
E	-	-	0.34	0.24	0.10	0.02	0.07	0.59	0.06
V-1	-	-	0.61	0.41	0.20	0.07	0.13	0.33	0.06
V-2	-	-	0.70	0.45	0.25	0.10	0.15	0.26	0.04
V-3	-	-	0.67	0.47	0.20	0.11	0.09	0.26	0.07
I-1	-	-	0.75	0.59	0.17	0.06	0.11	0.21	0.04
I-2	-	-	0.76	0.63	0.13	0.05	0.08	0.19	0.07
PSMC-67	0.80	82.2	0.73	0.29	0.44	0.23	0.21	0.22	0.05
-19	0.86	84.4	0.77	0.35	0.33	0.18	0.15	0.20	0.03
-34	0.75	83.9	0.77	0.42	0.35	0.19	0.16	0.20	0.03
-43	0.78	87.0	0.78	0.44	0.34	0.20	0.14	0.19	0.03
-47	0.73	88.0	0.86	0.43	0.43	0.26	0.16	0.12	0.02
-53	0.63	89.1	0.85	0.48	0.38	0.22	0.16	0.13	0.01
Aldwarke Silkstone									
Exinite	1.02	87.2	0.53	0.26	0.27	0.14	0.13	0.40	0.07
Vitrinite	0.75	86.9	0.80	0.38	0.42	0.21	0.21	0.15	0.05
Inertinite	0.48	92.1	0.89	0.59	0.30	0.17	0.13	0.10	0.01
Teversil Dunsil									
Vitrinite	0.75	81.5	0.78	0.30	0.48	0.23	0.25	0.18	0.04
Inertinite	0.53	87.7	0.86	0.37	0.49	0.21	0.28	0.12	0.02
Woolley Wheatley, Lime									
Exinite	0.95	87.9	0.47	0.29	0.18	0.09	0.09	0.46	0.07
Vitrinite	0.78	86.6	0.77	0.48	0.29	0.12	0.17	0.20	0.03
Inertinite	0.37	93.7	0.89	0.53	0.36	0.21	0.15	0.09	0.02
Markham Main									
Exinite	1.08	82.6	0.45	0.25	0.20	0.09	0.12	0.48	0.07
Vitrinite	0.80	82.2	0.76	0.33	0.41	0.23	0.18	0.21	0.06
Inertinite	0.47	91.6	0.82	0.51	0.31	0.18	0.13	0.15	0.03
North Celyen									
Exinite	0.65	90.6	0.84	0.40	0.44	0.27	0.17	0.14	0.02
Vitrinite	0.67	89.9	0.83	0.46	0.37	0.24	0.13	0.16	0.01
Inertinite	0.61	91.3	0.85	0.47	0.38	0.24	0.14	0.14	0.01
PSOC-1108	0.65	68.0	0.43	0.29	0.14	0.06	0.08	0.46	0.11
PSOC-1110	0.93	72.5	0.16	0.03	0.13	0.06	0.07	0.65	0.19
Beluga Lignite	0.94	65.7	0.64	0.17	0.47	0.07	0.40	0.25	0.11

$f_a = f_a^H + f_a^N = f_a^H + f_a^S + f_a^B$ $\qquad$ $f_s = f_s^H + f_s^*$

$f_a + f_s = 1$

f_s^* = Non-protonated aliphatic carbon plus methyl carbons.

Table III. Analytical Data for British Maceral Concentrates

Colliery	Woolley			Markham Main			Teversal			Aldwarke			North Celynen		
Seam	Wheatley Lime			Barnsley			Dunsil			Silkstone			Meadow Vein		
	V	E	I	V	E	I	V	E	I	V	E	I	V	E	I
H_2O, as anal., %	1.6	0.7	0.5	6.9	2.0	1.8	9.2	-	4.1	1.7	0.7	0.8	1.0	0.6	0.7
VM dmmf	36.1	57.8	9.0	40.1	73.7	18.1	35.1	-	21.5	33.2	66.5	15.4	24.4	22.2	19.4
C dmmf	86.6	87.9	93.7	82.2	82.6	91.6	81.5	-	87.7	86.9	87.2	92.1	89.9	90.6	91.3
H	5.6	6.9	2.9	5.5	7.4	3.6	5.1	-	3.9	5.4	7.4	3.7	5.0	4.9	4.6
N	1.8	1.1	0.4	1.9	1.1	0.4	2.0	-	1.1	1.8	1.2	0.7	1.6	1.4	1.2
S	1.1	1.1	0.2	1.1	1.6	(0.3)	0.6	-	0.4	0.73	0.6	0.4	0.68	(0.6)	(0.5)
O (diff.)	4.9	3.0	2.8	9.3	7.3	4.1	10.8	-	6.9	5.17	3.6	3.1	2.82	2.5	2.4
Rank	HVA	-	-	HVB	-	-	HVB	-	-	HVA	-	-	MVb	-	-
MM	1.4	2.8	4.9	1.4	0.9	6.0	0.4	-	2.9	0.8	0.3	5.0	2.9	4.5	8.87*
Vitrinite	96.0	10.0	4.0	98.0	3.0	6.0	98.0	-	6.0	98.0	0.0	4.0	86.0	40.0	15.0
Exinite	3.0	79.0	tr	tr	88.0	1.0	1.0	-	tr	1.0	95.0	-	3.0	30.0	11.0
Inertinite	1.0	11.0	96.0	2.0	9.0	92.0**	1.0	-	93.0*	1.0	5.0	96.0	11.0	30.0	71.0

* semifusinite

** equal amounts fusinite and semifusinite

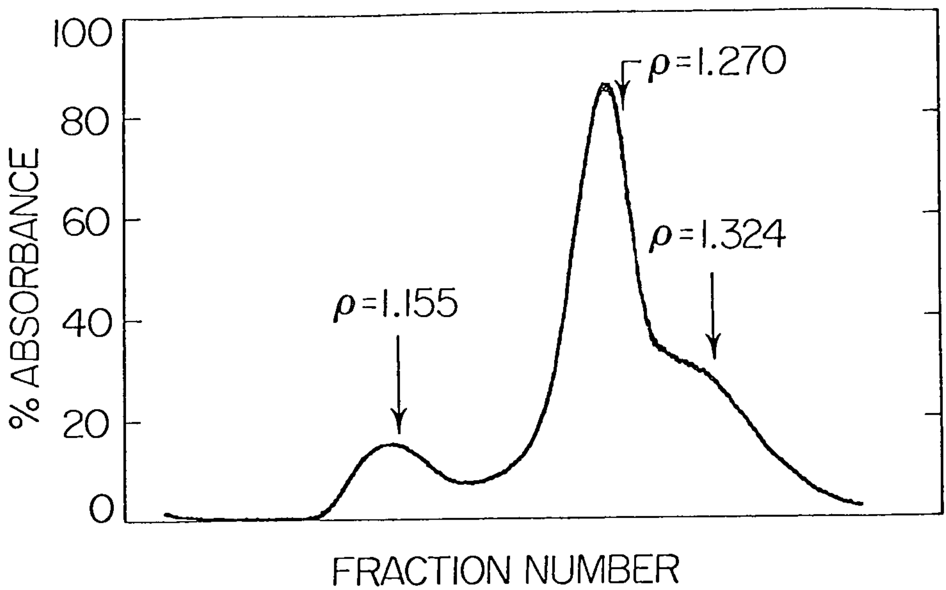

Figure 1. Fractogram for analytical DGC separation run on PSOC-2. The densities indicate the separation of the liptinite, vitrinite, and inertinite maceral groups.

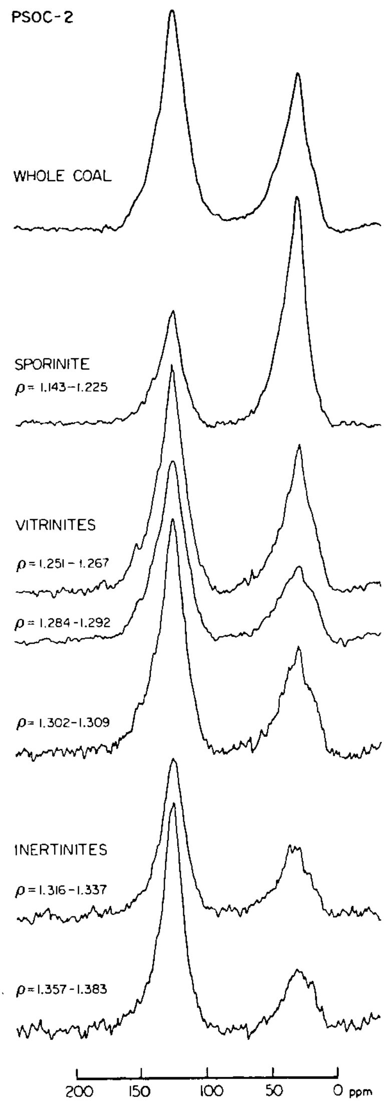

Figure 2. CP/MAS spectra of PSOC-2 whole coal and the maceral groups separated from the coal by density gradient centrifugation. The density ranges represent the range of densities for samples employed. f_a values are given for each sample.

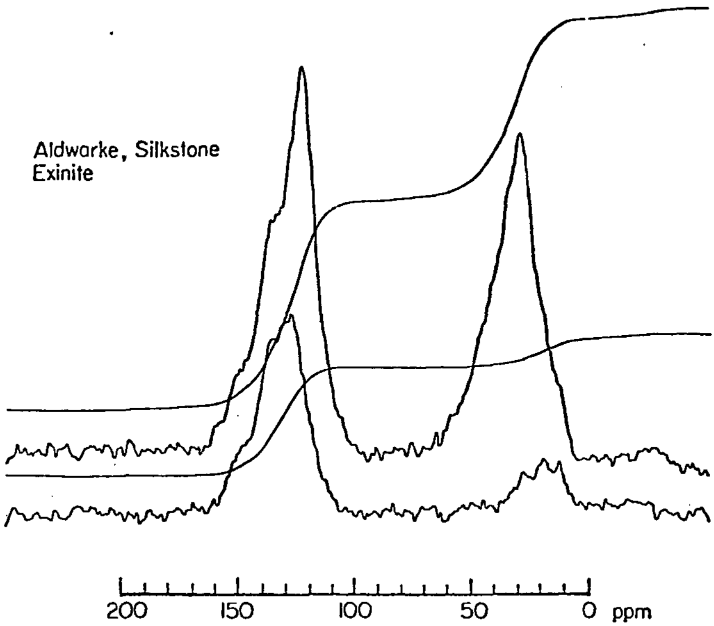

Figure 3. CP/MAS (top) and dipolar dephasing data with lower trace acquired following 40 μ sec. pulse delay. Note three separate peaks in the aliphatic region due to methyls and CH2's.

Aldworke, Silkstone Exinite

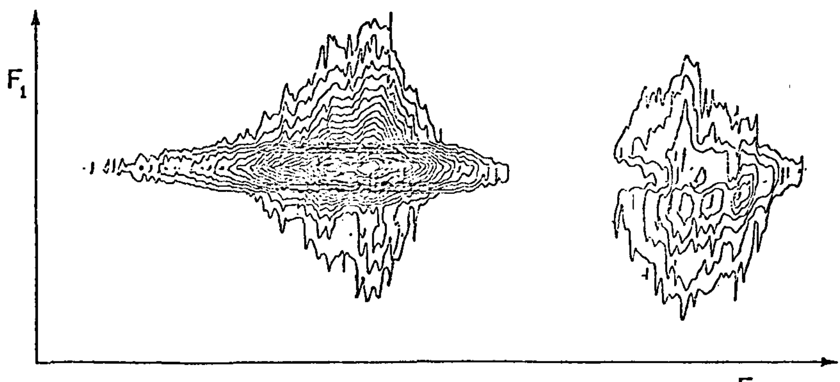

Figure 4. Contour plot for 2-D dipolar dephasing experiment.

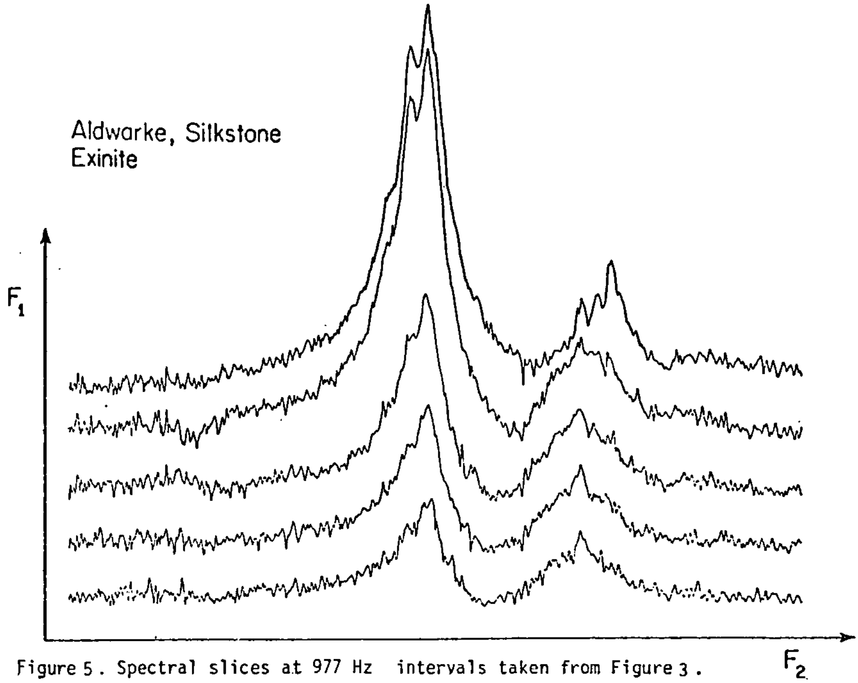

Figure 5. Spectral slices at 977 Hz intervals taken from Figure 3.

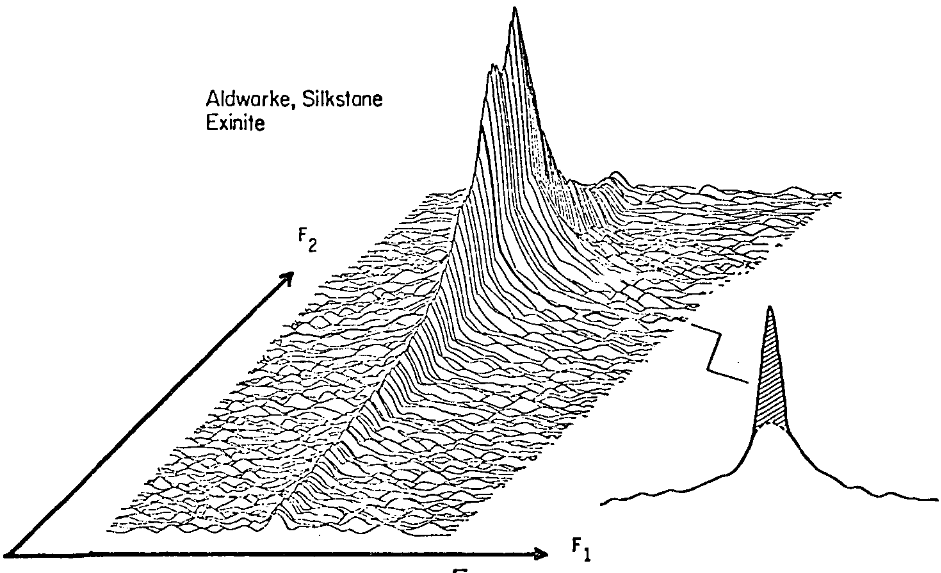

Figure 6. Three dimensional plot of aromatic region. Shaded portion is non-protonated carbon on top of resonance from protonated aromatic carbon. PUG 19